Tetraferrocenyl[5]cumulene, (Fc)₂C=C=C=C=C(Fc)₂: Synthesis, Electrochemistry, and Reactivity, Including Nickel(0)-Promoted [3]Ferrocenophane Formation and [2+2] Cycloaddition with Fullerene C₆₀

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Tetraferrocenyl[5]cumulene (Fc)₂C=C=C=C=C(Fc)₂ (Fc = ferrocenyl) is synthesized from 1,1-diferrocenyl-1-methoxypropyne by formal dimerization of diferrocenylethenylidenecarbene generated in situ by deprotonation and elimination of methoxide. The cumulene is an air-stable compound of blue color with an electron-rich cumulene moiety, as indicated by various spectroscopic methods. In contrast to other (shorter) ferrocenyl cumulenes which show no reactivity due to steric hindrance, (Fc)₂C=C=C=C=C(Fc)₂ is a quite reactive compound, as exemplified by (i) transition metal complex formation with Rh(I), (ii) [3]ferrocenophane generation by Ni(0)-promoted intramolecular electrophilic aromatic substitution, and (iii) [2+2] cycloaddition with olefins and alkynes, and (iv) [2+2] cycloaddition with C₆₀ and C₇₀, yielding the first cumulene derivatives of fullerenes. MS, UV−vis, IR, Raman, NMR, cyclic voltammetry, controlled potential coulometry, Mössbauer spectroscopy, and X-ray single-crystal structure analysis have been performed to characterize the new compounds.

Introduction

Cumulated sp carbon chains with electroactive end groups are currently under active investigation due to their potential use as molecular wires and other nanoelectronic devices. Most work in this area is focused on the chemical and physical properties of metallacumulenes[1−4] [M]=Cₙ=[M] with late transition metal termini and with acetylenic/cumulenic bridging carbon ligands. Conceptually, these metallacumulenes can be envisaged as elongated and unsaturated Fischer carbene[5,6] complexes, and synthetically, such compounds are relatively easily accessible by modern ethynyl cross-coupling reactions.[7−9]

In comparison to the very large number of known metallacumulenes,[1] the alternative concept of combining an organic cumulenic bridging subunit with electroactive organometallic substituents has been explored only very little in this context. Our contribution to this field has been the preparation and characterization of a series of ferrocenyl cumulenes (Fc)₂Cₙ(Fc)₂ with up to five cumulated carbons,[10−15] and in this report we summarize our results on the next member in this series, tetraferrocenyl[5]cumulene (Fc)₂C=C=C=C=C(Fc)₂. The ferrocenyl substituents have been chosen because of their (i) highly stable and reversible Fe(II)/Fe(III) redox couple,[16] (ii) high donor capacity with regard to the anchimeric stabilization of adjacent carbenium centers,[14] and (iii) steric bulk, which might allow the preparation, isolation, and study of longer cumulenes (i.e., Cₙ with n > 6), which have been shown to be unstable and not isolable with purely organic substituents.[17,18] Accordingly, the combined steric bulk of the four ferrocenyl termini prevented any chemical reactiv-

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Scheme 1.   Synthesis of Compounds 1−3 (Fc = ferrocenyl)
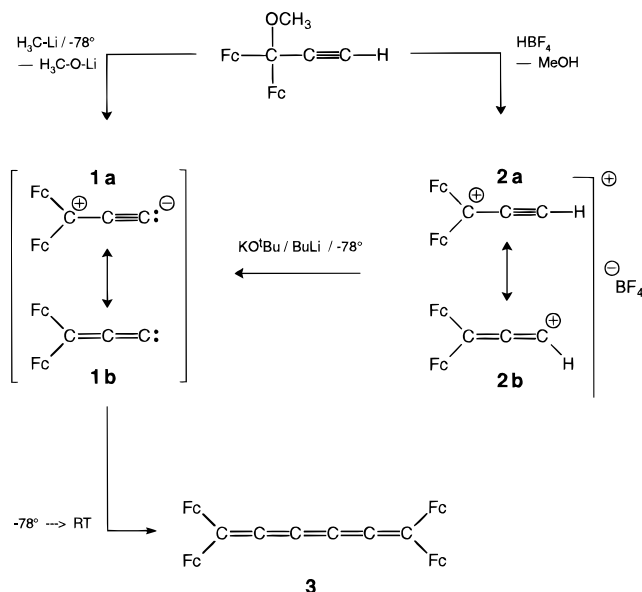
ity of the electron-rich cumulene subunit in the case of the shorter cumulenes in this series (tetraferrocenyl-ethylene,[15] -allene,[13] and -butatriene[11]), in contrast to the longer systems, tetraferrocenyl[4]cumulene[10] and tetraferrocenyl[5]cumulene, the main target compound of the present paper. The chemical reactivities that have been studied and on which will be reported in the following include complex formation, metal-assisted radialene formation, and [2+2] cycloaddition reactions, most notably with fullerenes C_{60} and C_{70}.

Results and Discussion

Synthesis and Properties of Tetraferrocenyl[5]-cumulene. In contrast to the shorter [2]-, [3]-, and [4]-cumulenes, hexapentaenes ([5]cumulenes) are in general more easily accessible,[17,18] either by reduction of the corresponding hexadiynediols[19] or by formal dimer-ization or self-condensation of ethenylidenecarbenes.[20,21] The latter method of synthesis was also applicable to the preparation of tetraferrocenylhexapentaene **3**, al-though under modified conditions in comparison to the classical[20,21] synthesis. Starting from diferrocenylmeth-oxypropyne,[10,11] which is a very useful O-protected propargylic synthon, two pathways lead to the desired cumulene **3** (Scheme 1).

First, deprotonation of diferrocenylmethoxypropyne with concomitant elimination of methoxide forms zwit-terion **1a** and the corresponding diferrocenylethenyliden-ecarbene **1b**, respectively, which formally dimerizes to give **3**. It has been shown earlier that (i) such carbenes have only fleeting existence with considerable zwit-

terionic character[22] and (ii) the formal dimerization of such unsaturated carbenes occurs most likely via the nucleophilic addition of a propargylic anion to the ethenylidenecarbene with subsequent elimination of the propargylic O-leaving group.[21]

Second, acid-promoted elimination of methanol from diferrocenylmethoxypropyne afforded 1,1-diferrocenyl-prop-2-yn-1-ylium tetrafluoroborate **2a,b** as an air-sensitive but still stable and isolable green ($\lambda_{max} = 738$ nm) salt. We have shown earlier that ferrocenyl sub-stituents in general are very efficient stabilizing groups for conjugated unsaturated carbenium species,[14] and the existence of **2a,b** with an unsubstituted alkyne group gives further proof of this property of metallocenyl groups. However, the spectroscopic data of **2a,b** indicate that the cumulene structure **2b** is of negligible impor-tance, as evidenced most clearly by the observation of a weak alkyne band ($\nu_{C\equiv C} = 2093$ cm^{-1}) in direct comparison to triferrocenylallenylium tetrafluorobo-rate,[14] $(Fc)_2C=C=C(Fc)^+BF_4^-$, which has a very intense IR cumulene vibration ($\nu_{C=C=C} = 2151$ cm^{-1}). In addi-tion, the ^1H and ^{13}C NMR chemical shifts of **2a,b** are almost identical to those of simple diferrocenylmethy-lium salts $(Fc)_2CH^+X^-$,[23] suggesting predominance of structure **2a**. Deprotonation of **2a** with potassium tertiary butoxide generated the intermediate diferroce-nylethenylidenecarbene **1b** and finally tetraferrocenyl-hexapentaene **3** as described above, albeit in low yield. In terms of ease of synthesis and yield of product, the first pathway, in situ deprotonation of diferrocenyl-methoxypropyne and elimination of methoxide, is there-fore the method of choice for the preparation of **3**. Optimized conditions for this reaction include the use of an excess of methyllithium as base and diethyl ether as solvent with careful control of the progress of the reaction by TLC analysis; use of other reagents or other stoichiometries and longer reaction periods resulted in reduced yields and/or unseparable product mixtures.

Tetraferrocenyl[5]cumulene **3** is an air-stable com-pound (mp 112 °C, dec) of dark blue color ($\lambda_{max} = 624$ nm, $\epsilon = 22500$), in contrast to other organic [5]cumu-lenes, which are orange to red,[17,18] reflecting the elec-tronic interaction between the four ferrocenyl termini and the bridging cumulene ligand. Figure 1 shows a comparison of the UV−vis spectra of tetraferrocenylcu-mulenes with two to six cumulated carbons, illustrating the expected bathochromic shift and increase of the molar extinction coefficient ϵ with increasing length of the cumulene chain. Particularly interesting is the fact that cumulenes with an *even* number of carbons (C_2, C_4, C_6) and an *odd* number of cumulated bonds (tetrafer-rocenyl[1]-, [3]-, [5]cumulene), respectively, show their λ_{max} at much higher wavelengths in comparison to cumulenes with an *odd* number of carbons (C_3, C_5) and an *even* number of cumulated bonds (tetraferrocenyl-[2]-, [4]cumulene), respectively. The difference between odd (C=C=C, C=C=C=C=C) and even (C=C=C=C, C=C=C=C=C=C) cumulenes in terms of the degree of conjugation is due to the orthogonality of the π-planes of the terminal carbons in the case of odd-numbered

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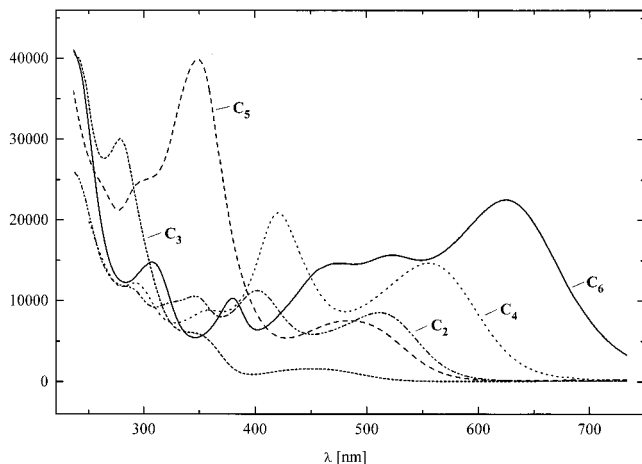
Figure 1. UV–vis spectra of tetraferrocenylcumulenes $(Fc)_2C_n(Fc)_2$ with $n = 2, 3, 4, 5, 6$.

Figure 2. Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4]$-$[PF_6]$ (0.2 mol/L) and (a) **3** (6×10^{-4} mol/L); (b) tetraphenyl[5]cumulene (1×10^{-3} mol/L). Scan rate 0.2 V s^{-1}. Inset: a detail of the first oxidation of **3** at 0.05 V s^{-1}. $T = -10$ °C.

cumulenes (C_3, C_5), which prevents conjugation between the two pairs of substituents.[24,25]

Raman spectroscopy of **3** showed an intense cumulene vibration $\nu_{C=C=C=C=C=C} = 1973$ cm^{-1}, comparable to the corresponding cumulenic band of the metallacumulene $[Re]=C_4=[Re]^{2+}$ ($\nu_{Re=C=C=C=C=Re} = 1883$ cm^{-1}) reported recently by Gladysz et al.[26] The ^1H and ^{13}C NMR spectral parameters of **3** are in accord with regular, undistorted, and magnetically equivalent ferrocenyl substituents, indicating the existence of only one species in solution. Usually two ferrocenyl substituents bonded to a sp^2 carbon are arranged in an up–down fashion[10,11,13,15] with slightly tilted Cp planes to minimize steric interaction between the inner ortho hydrogens of the substituted Cp rings, and as a consequence, cis–trans (syn–anti) isomers with regard to the C=C=C=C=C=C bridging moiety can be envisaged. These are obviously not observed in the NMR spectra, suggesting free pairwise rotation of the four ferrocenyl substituents in solution. In this context it is interesting to note that 1,6-diphenyl-1,6-di-*tert*-butyl[5]cumulene[27] is the only known example where cis–trans isomers of a [5]cumulene have been observed. In consonance with the symmetry of the molecule, the six carbons of the cumulene subunit of **3** give rise to three ^{13}C NMR signals ($\delta = 119.8, 119.9, 140.8$ ppm) with rather unexceptional chemical shift values, analogous to the case of shorter ferrocenyl cumulenes.[10,11,13,15] In accord with the diamagnetism and hence clean NMR spectra of **3**, ^{57}Fe Mössbauer spectroscopy showed an isomer shift and quadrupole splitting typical of Fe(II), similar to other ferrocenyl-substituted cumulene compounds.[12] Further structural proof of cumulene **3** would include a single-crystal structure analysis, but unfortunately all our attempts to obtain suitable crystals were in vain.

Figure 2a shows the cyclic voltammogram of cumulene **3** in dichloromethane solution, at $T = -10$ °C. The most obvious interpretation that the four ferrocene

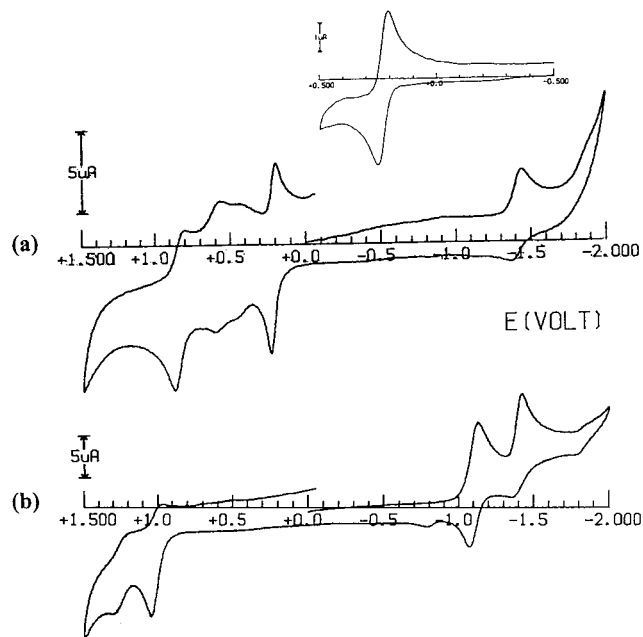(24) Irngartinger, H.; Götzmann, W. *Angew. Chem.* **1986**, *98*, 359; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 340.
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subunits undergo two separate two-electron oxidations is not supported by the comparison with the cyclic voltammetric response exhibited by the related tetraphenyl[5]cumulene, Figure 2b.

As a matter of fact, tetraphenyl[5]cumulene undergoes two separate reductions and one main oxidation. Controlled potential coulometry performed in correspondence to the first cathodic step ($E_w = -1.2$ V) consumes two electrons/molecule. Cyclic voltammetric tests on the solution resulting from exhaustive two-electron reduction prove that during the long durations of macroelectrolysis at room temperature the electrogenerated dianion is only partially stable. Hence on the basis of the relative peak heights, tetraphenyl[5]cumulene undergoes (i) two separate two-electron reductions, the first one being chemically reversible and the second one being partially reversible in the cyclic voltammetric time scale and (ii) a partially reversible two-electron oxidation. On this basis, we can state that **3** undergoes a first ferrocene-based four-electron oxidation at $E^{o\prime} = +0.23$ V (which is more clearly visible in the inset of Figure 2a), followed by a cumulene-centered two-electron oxidation at $E^{o\prime} = +0.83$ V, as well as a cumulene-centered two-electron reduction at $E^{o\prime} = -1.39$ V. Even if we did not succeed in confirming the consumption of four electrons in the ferrocene-based oxidation by controlled potential coulometry because of electrode adsorption phenomena, the above assignment agrees well with the results previously obtained for the ferrocene-based oxidation processes in the series $(Fc)_2C_n(Fc)_2$: $n = 2$, four separate one-electron oxidations;[15] $n = 3$, two separate one-electron oxidations followed by a further two-electron oxidation;[13] $n = 4$, two two-electron oxidations separated by $\Delta E^{o\prime} = 0.16$ V;[11] $n = 5$, two two-electron oxidations separated by $\Delta E^{o\prime} = 0.09$ V.[10] Such a trend indicates that with increasing length of the

Table 1. Formal Electrode Potentials (V, vs SCE) for the Redox Changes Exhibited by 3 and $(C_6H_5)_2C_6(C_6H_5)_2$ in Dichloromethane Solution ($T = -10$ °C)

| | ferrocene-based oxidation | | cumulene-based processes | | | |
| | | | 2e⁻ oxidation | 2e⁻ reductions | | |
complex	$E°'_{4+/0}$	$\Delta E_p{}^a$	$E_p{}^b$	$E°'$	$\Delta E_p{}^a$	$E_p{}^{a,b}$
$(C_6H_5)_2C_6(C_6H_5)_2$			+1.02	−1.11	74	−1.43
$(Fc)_2C_6(Fc)_2$ (**3**)	+0.23	66	+0.83	−1.39	98	c
FcH	+0.35	75				

^{a} Measured at 0.1 V s⁻¹. ^{b} Peak potential values for processes coupled to chemical complications. ^{c} Close to the solvent discharge.

bridging cumulated carbon chain the electronic communication among the ferrocene units decreases until it disappears in the actual hexapentaene spacer. It deserves attention that the solution resulting from (electrode poisoning) exhaustive oxidation at +0.4 V no longer displays in cyclic voltammetry traces of the original profile, thus indicating that the present ferrocenium tetracation is not stable during the long durations of macroelectrolysis. Finally, it is interesting to note from Table 1 that the ferrocenyl groups in **3** are more easily oxidized by about 0.12 V with respect to free ferrocene, in consonance with electron donation by the cumulene bridge toward the ferrocenyl termini. On the other hand, the ferrocenyl donors have the expected influence on the redox processes of the cumulene subunit, as evidenced by a facilitated cumulene-based oxidation [+0.83 V for **3** vs +1.02 V for $(C_6H_5)_2C_6(C_6H_5)_2$] and a more difficult cumulene-based reduction [−1.39 V for **3** vs −1.11 V for $(C_6H_5)_2C_6(C_6H_5)_2$], respectively.

Reactivity of Tetraferrocenyl[5]cumulene. We have shown earlier[11,13,15] that "shorter" tetraferrocenylcumulenes $(Fc)_2C_n(Fc)_2$ with $n = 2, 3, 4$ are unreactive because of steric hindrance by the four ferrocenyl termini. In contrast, **3** is an electron-rich cumulene that reacts with (i) transition metals, (ii) olefins, (iii) alkynes, and (iv) fullerenes to form the corresponding metal complexes, rearranged products, and cycloadducts, respectively.

(a) Protonation. A first indication of the basicity or nucleophilicity of **3** is its facile reaction with Bronsted acids. Addition of HBF₄ to a solution of **3** results in an immediate color change from blue to green, indicating formation of C(2)-protonated 1,1,6,6-tetraferrocenyl-2,3,4,5-tetraen-1-ylium tetrafluoroborate. The high stability or ease of formation of this salt is due to the α-carbenium stabilizing effect of the ferrocenyl groups, similar to that in other conjugated ferrocenyl carbenium systems.[10,14] This reactivity with its noticeable color change can be used for convenient detection of **3** on TLC plates by simply exposing the developed plates to HCl vapor.

(b) Coordination Chemistry. Transition metal complexes of organic [5]cumulenes are comparatively rare. Only a limited number of transition metal fragments, including Fe(CO)₄, Fe₂(CO)₆, Pt(PR₃)₂, and RhCl(PR₃)₂, have been reported to yield stable [5]cumulene complexes.[28−31] Therefore it was of interest to explore

the coordination chemistry of tetraferrocenyl[5]cumulene **3** in direct comparison to aliphatic[28] or aromatic[29,31] organic cumulenes (Scheme 2). Reaction of **3** with Fe₂(CO)₉ gives—in addition to decomposition of the starting material as the main reaction—a number of products in very low yield, most likely a mixture of [(Fc)₂C₆(Fc)₂]-Fe(CO)₄ and [(Fc)₂C₆(Fc)₂]Fe₂(CO)₆ according to IR spectral analysis, similar to the analogous reaction of aliphatic [5]cumulenes.[28] Because of the disappointing low yield of this reaction and, more important, because of difficulties in separating and purifying the products, no further information on this reaction is available. Similarly, reactions with Pt(PR₃)₄, AuCl(CO), IrCl(CO)-(PR₃)₂, and CoCp(CO)₂ all yielded new products that were formed either in too low a yield or in an admixture with unseparable byproducts, thus preventing the identification of any characteristic properties.

In marked contrast, interaction of cumulene **3** with RhCl(PR₃)₃ in refluxing benzene yielded a dark purple, air-stable complex **4** in 48% yield (Scheme 2). FAB mass spectroscopy clearly established that a complex of formula RhCl(PR₃)₂[(Fc)₂C₆(Fc)₂] was formed by observation of the corresponding molecular ion M⁺ with $m/z = 1474.5$.

As has been observed before in three other Rh(I)−[5]-cumulene complexes,[29−31] the metal is η^2-coordinated to the C(2)−C(3) π-bond of the cumulene chain, forming an unsymmetrical complex with regard to the cumulene ligand. Accordingly, the four ferrocenyl substituents are magnetically nonequivalent with the corresponding number of signals in the ¹H and ¹³C NMR spectra. The ¹³C NMR signals of the six cumulene carbons are observed at 107.9, 114.0, 122.6, 123.9, 132.3, and 153.5 ppm, and five of these six carbons are magnetically coupled as doublets to ¹⁰³Rh with coupling constants ranging from 19 to 3 Hz, in addition to further couplings as triplets to ³¹P. ³¹P NMR shows one signal with coupling to Rh ($\delta = 27.1$ ppm, d, $^1J(^{31}P-^{103}Rh) = 125.7$ Hz), indicating magnetic equivalence of the two phosphine ligands in this four-coordinated Rh(I) complex, in consonance with data of comparable organic cumulene Rh complexes.[29−31] A single-crystal structure analysis (Table 2, Figure 3) gives definite proof of these structural assignments.

The rhodium is in a square-planar coordination environment with two trans triphenylphosphine ligands. The η^2-bonded cumulene ligand is considerably bent [C(1)−C(2)−C(3) = 146.9(9)°; C(2)−C(3)−C(4) = 151.8-(9)°; C(3)−C(4)−C(5) = 179.4(9)°; C(4)−C(5)−C(6) = 171.5(10)°], and the cumulene subunit C=C=C=C=C=C shows alternating bond distances [C(1)−C(2) = 138.5-(13); C(2)−C(3) = 129.9(13); C(3)−C(4) = 136.9(13); C(4)−C(5) = 123.4(12); C(5)−C(6) = 137.7(13) pm], similar to what was reported for three other crystal structures of [5]cumulene Rh(I) complexes.[29−31] All four ferrocenyl substituents are in the preferred up−down conformation with slightly tilted ferrocenyl groups with respect to each other, thereby minimizing steric congestion. Further relevant bond distances and angles are listed in the caption of Figure 3.

**(c) Cycloadditions.** The only known organic cycloaddition chemistry of [5]cumulenes is their thermal

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Scheme 2.   Synthesis of Compounds 4−7 (Fc = ferrocenyl)
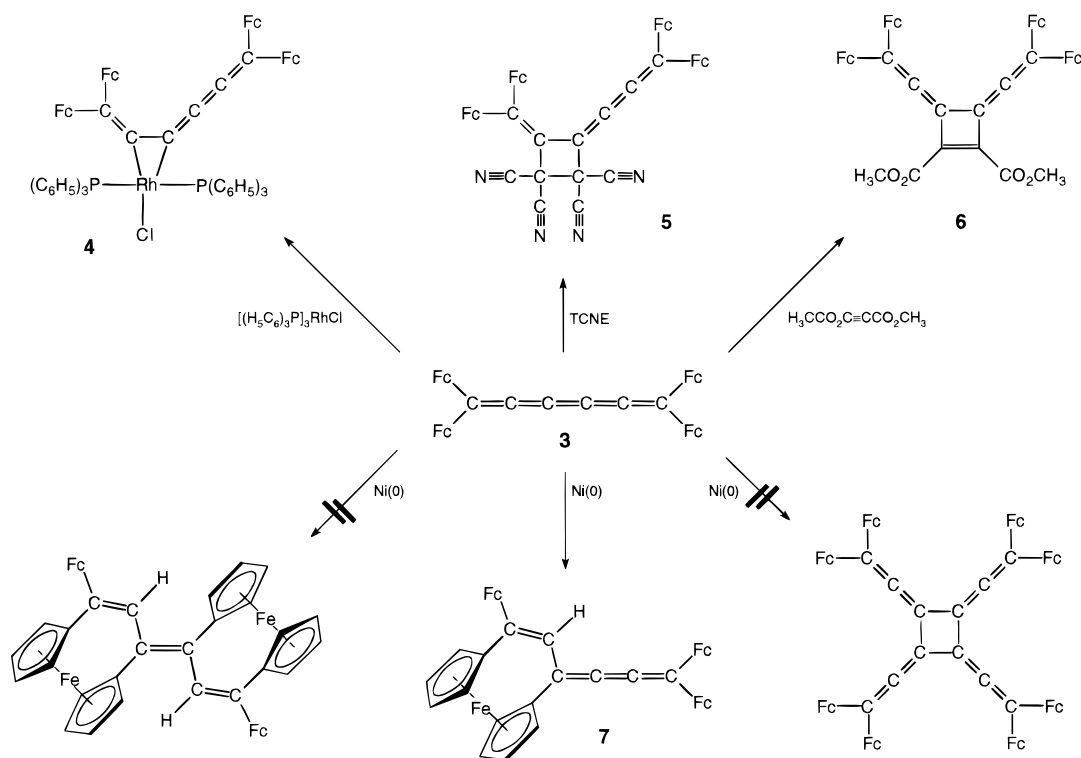
[2+2] cyclodimerization to yield symmetric or unsymmetric radialenes.[32] Radialenes are intriguing molecules with very interesting redox properties;[33] therefore the posssible incorporation of eight additional redox centers via formation of octaferrocenyl-substituted [4]radialenes by cyclodimerization of tetraferrocenyl[5]cumulene **3** was an exciting prospect. However, only decomposition but no reaction in terms of a new isolable product was observed when cumulene **3** was heated to 200 °C, either in solution or without solvent. In retrospect, this is not too surprising because it has been shown that only acceptor-substituted cumulenes cyclodimerize with thermal activation,[33] and tetraferrocenyl[5]cumulene **3** is obviously a donor-substituted cumulene. We also note that attempted cyclodimerization with photochemical activation failed.

To further probe the reactivity of **3**, we investigated the interaction of **3** with common organic activated (acceptor-substituted) dienophiles (Scheme 2). The highly electron-deficient and strongly electrophilic tetracyanoethylene (TCNE)[34,35] reacts instantaneously with **3**, affording [2+2]-cycloadduct **5**. The regioselective formation of this unsymmetric cycloadduct is clearly established by observation of the corresponding number of signals in the ^{1}H and ^{13}C NMR spectra for the four magnetically nonequivalent ferrocenyl and cyano substituents in addition to six ^{13}C signals for the former C=C=C=C=C=C subunit. Similarly, reaction of **3** with dimethyl acetylenedicarboxylate afforded [2+2]-cycloadduct **6**, although 3 days of reflux in benzene proved necessary in comparison to the very fast reaction

between **3** and TCNE. In contrast to the unsymmetric product **5**, in cycloadduct **6** the central π-bond, C(3)−C(4), is involved in carbacyclic ring formation, most likely because of steric hindrance by the more voluminous methyl ester substituents as compared to the cyano groups of TCNE. It is interesting to note that compound **6** with two diferrocenylallene units has a dark blue color (λ_{max} = 750 nm), whereas most unsymmetric compounds with a diferrocenylbutatriene subunit attached to an acceptor moiety [e.g., C(2)-protonated **3** (see above), unsymmetric cycloadduct **5**, fullerene adduct **8b** (see in the following)] have a dark green color. The structural assignment of cycloadduct **6** is corroborated by its ^{1}H and ^{13}C NMR spectra, which show fewer signals in comparison to unsymmetric **5** and in consonance with possible C_{2v} or D_{2h} symmetry.

(d) Ni(0)-Promoted Ferrocenophane Formation. A general synthesis of [4]radialenes is the zerovalent metal-promoted cyclodimerization of [5]cumulenes,[33] usually with Ni(0) compounds. With this goal in mind we reacted tetraferrocenyl[5]cumulene **3** with various Ni(0) complexes, and indeed a new stable product of red color was isolable in 36% yield (Scheme 2). However, according to mass spectroscopy, none of the desired octaferrocenyl[4]radialene was formed; instead cumulene **3** has been transformed to an unusual [3]ferrocenophane **7**. In general, ferrocenophanes are an intriguing class of compounds with unusual properties,[36,37] but formation of a [3]ferrocenophane starting from a [5]-cumulene is without precedent. ^{1}H and ^{13}C NMR spectroscopy of **7** indicated the occurrence of only three unsubstituted cyclopendienyls in addition to complex multiplets in the ^{1}H NMR spectrum and an unexpected

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Table 2. Crystal Data and Structure Refinement for 4 and 7

	4	7
mol formula	$C_{82}H_{66}ClFe_4P_2Rh$	$C_{46}H_{36}Fe_4$
fw	1475.05	812.15
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 1)
a (pm)	2119.7(6)	1213.6(2)
b (pm)	1231.4(2)	1296.6(2)
c (pm)	2512.8(6)	1368.6(2)
α (deg)	90	118.08(1)
β (deg)	97.92(2)	110.53(1)
γ (deg)	90	93.76(1)
V (nm³)	6.496(3)	1.7087(4)
Z	4	2
temp (K)	213(2)	213(2)
d (calcd) (Mg/m³)	1.508	1.579
abs coeff (mm⁻¹)	1.258	1.699
$F(000)$	3016	832
color, habit	deep red prism	red prism
cryst size (mm)	0.5 × 0.3 × 0.25	0.4 × 0.21 × 0.11
θ range for data collcn (deg)	2.55−22	3.02−23.00
index ranges	$0 \leq h \leq 22$	$0 \leq h \leq 12$
	$0 \leq k \leq 12$	$-11 \leq k \leq 11$
	$-26 \leq l \leq 26$	$-15 \leq l \leq 15$
no. of rflns collcd	8024	4557
no. of indep rflns	7779 ($R_{int} = 0.0996$)	4557 ($R_{int} = 0.0000$)
no. of rflns with $I > 2\sigma(I)$	5496	3788
abs corr	none	Ψ-scan
max and min transm		0.970 and 0.832
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	6888/0/401	4380/3/497
goodness-of-fit on F^2	1.004	1.029
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0887$	$R_1 = 0.0542$
	$wR_2 = 0.2173$	$wR_2 = 0.1205$
R indices (all data)	$R_1 = 0.1267$	$R_1 = 0.0714$
	$wR_2 = 0.2838$	$wR_2 = 0.1333$
max diff peak/hole (e·nm⁻³)	1372 and −1907	674 and −434

Figure 3. Molecular structure of **4**. Hydrogens and five carbons of each phenyl group of the two triphenylphosphine ligands are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19), for ferrocene 2 C(20)−C(29), for ferrocene 3 C(30)−C(39), and for ferrocene 4 C(40)−C(49), respectively. Selected bond distances (pm): C(1)−C(2) = 138.5(13); C(2)−C(3) = 129.9(13); C(3)−C(4) = 136.9(13); C(4)−C(5) = 123.4(12); C(5)−C(6) = 137.7(13); Rh(1)−C(2) = 203.2(10); Rh(1)−C(3) = 202.8(9); Rh(1)−P(1) = 235.3(3); Rh(1)−P(2) = 234.9(3); Rh(1)−Cl(1) = 237.0-(3). Selected bond angles (deg): C(1)−C(2)−C(3) = 146.9-(9); C(2)−C(3)−C(4) = 151.8(9); C(3)−C(4)−C(5) = 179.4(9); C(4)−C(5)−C(6) = 171.5(10); P(1)−Rh(1)−P(2) = 172.89-(9); C(2)−Rh(1)−C(3) = 37.3(4); P(1)−Rh(1)−Cl(1) = 88.16-(9); P(2)−Rh(1)−Cl(1) = 85.16(9).

Figure 4. Molecular structure of **7**. Hydrogens [except for H on C(5)] are omitted for clarity, and only molecule A is shown. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19), for ferrocene 2 C(20)−C(29), for ferrocene 3 C(30)−C(39), and for ferrocene 4 C(40)−C(49), respectively. Selected bond distances (pm): C(1)−C(2) = 138(2); C(2)−C(3) = 125(2); C(3)−C(4) = 134(2); C(4)−C(5) = 152(2); C(5)−C(6) = 133(2). Tilt angle of plane Cp[C(10)−C(11)−C(12)−C(13)−C(14)] vs plane Cp[C(15)−C(16)−C(17)−C(18)−C(19)] = 12.6(1.6)°.

large number of nonequivalent carbon resonances in the ¹³C NMR spectrum. Luckily, X-ray quality single crystals could be obtained, which allowed unambiguous structural proof for **7** (Figure 4, Table 2).

The ferrocenophane part of the molecule is a 1,1′-disubstituted ferrocene Fe(3) with a three-membered unsaturated bridge C(4)−C(5)−C(6). In comparison to the common coplanar arrangement of the cyclopentadienyl rings in almost all ferrocene compounds, the C_3-bridging unit [C(4)−C(5) = 152(2); C(5)−C(6) = 133(2) pm] forces the two Cp rings of ferrocene Fe(3) slightly out of coplanarity [tilt angle: 12.6(1.6)° for molecule A and 10.0(1.5)° for molecule B, respectively]. The butatriene subunit C(1)−C(2)−C(3)−C(4) is almost linear, as anticipated with two longer terminal bonds [C(1)−C(2) = 138(2); C(3)−C(4) = 134(2) pm] and a shorter central bond [C(2)−C(3) = 125(2) pm].

One might speculate on the mechanism of the formation of ferrocenophane **7** from cumulene **3**. Most likely, Ni(0) coordinates to the π-bond C(4)−C(5), forming an intermediate unstable complex analogous to Rh(I) complex **4**. This leads to some electron-deficiency at both carbons C(4) and C(5), which makes them both electrophilic, but only carbon C(4) is in a preferential position to react with one of the two ferrocenyl substituents on carbon C(6) by an intramolecular aromatic electrophilic substitution. One might also speculate (compare Scheme
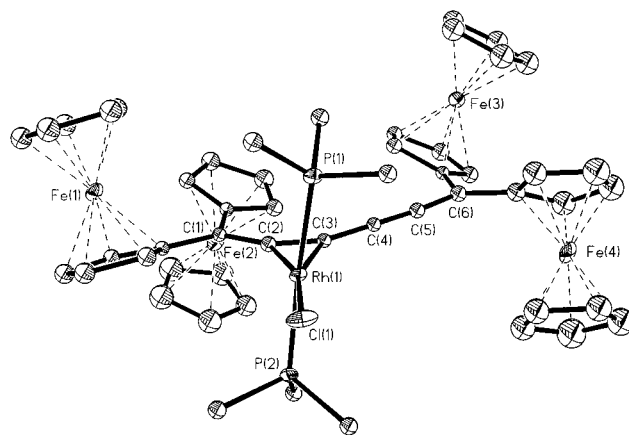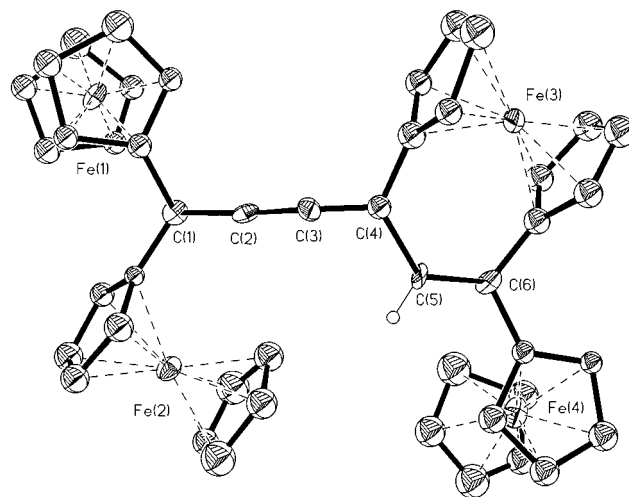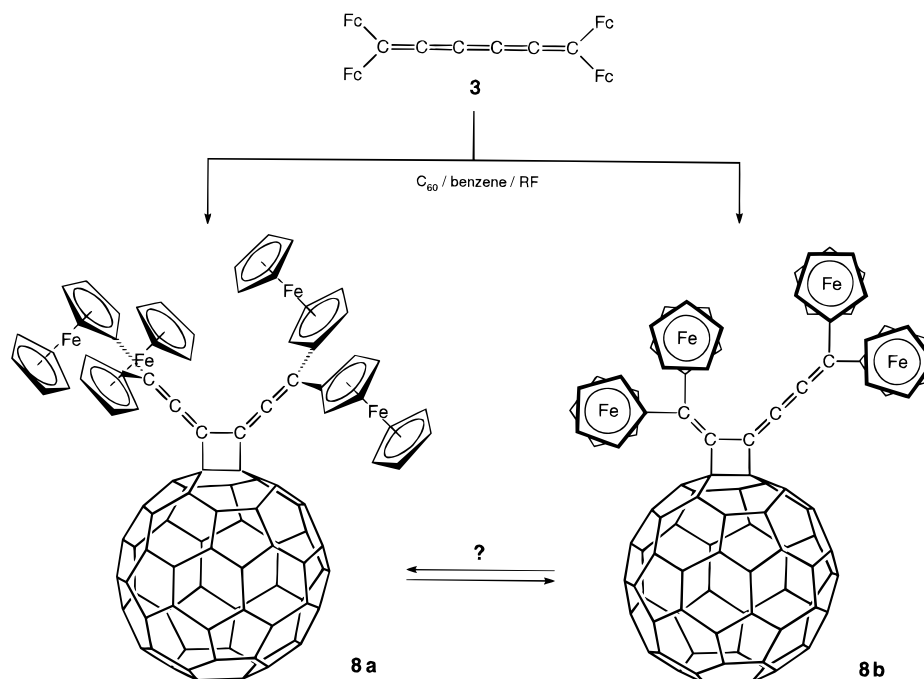
2) that this intramolecular substitution could occur a second time with compound **7** as the substrate, but even extended treatment of cumulene **3** or ferrocenophane **7** with different Ni(0) sources never yielded any new product, indicating reduced basicity of the four-carbon cumulene ligand of **7** as compared to the six-carbon cumulene bridge in **3**. We also tried to use AlCl₃ instead

Scheme 3. [2+2] Cycloadditions of Cumulene 3 with C_{60} (Fc = ferrocenyl)

of Ni(0) as the catalyst for this intramolecular aromatic electrophilic substitution, but only Ni(0) was effective.

(e) Fullerene Functionalization. The successful [2+2] cycloaddition of cumulene **3** with acceptor-substituted organic dienophiles to yield compounds **5** and **6** was the stimulus to try an analogous reaction with fullerene C_{60} as the acceptor component. At this point it is noteworthy that shorter ferrocenylcumulenes $(Fc)_2C_n(Fc)_2$ with $n = 2, 3, 4$ whose cumulene moiety is effectively shielded by the four bulky ferrocenyl substituents only form clathrates[11] with C_{60}, similar to the cocrystallization of C_{60} and C_{70} with ferrocene.[38,39] In marked contrast, cumulene **3** does indeed react with fullerene (Scheme 3): refluxing a blue benzene solution of **3** with C_{60} yields a green solution, indicating [2+2] cycloaddition at a 6,6-ring junction of C_{60}. The isolated green crude product mixture was analyzed by FAB mass spectroscopy and showed a parent peak ($m/z = 1534$, $M^+ + H$) corresponding to a 1:1 cycloadduct of C_{60} with **3**. However, further purification by chromatography allowed the separation of a less soluble product fraction which probably consists of bis-, ter-, and higher adducts, but no mass spectral confirmation was possible, either because of degradation (cycloreversion) in the gas phase or due to insufficient solubility in the nitrobenzyl alcohol matrix.

The soluble monoadduct fraction was shown by ^{1}H NMR spectroscopy to consist of a mixture of two regioisomers, **8a** (two magnetically equivalent ferrocenyl groups) and **8b** (four magnetically nonequivalent ferrocenyl groups), with respect to [2+2] cycloaddition at the π-bonds of the C(3)−C(4) and C(2)−C(3) carbons of cumulene **3**. In principle, the relative orientation of the two pairs of ferrocenyl substituents allows the existence of two isomers for the symmetric C(3)−C(4) adduct,

either with C_{2v} (isomer **8a** shown in Scheme 3) or with D_{2h} symmetry (not shown in Scheme 3). Inspection of Darling models[40] showed steric congestion of the latter isomer with D_{2h} symmetry due to very close contacts of the two symmetry-related syn ferrocenyl substituents; therefore we assign structure **8a** to the symmetric [2+2] cycloadduct of cumulene **3** with C_{60}. One might speculate that **8a** is the kinetic product of this cycloaddition reaction because of the more facile interaction of the C_{60} carbon sphere with cumulene **3**, and **8b** can be considered as the thermodynamically more stable product because of the higher electron density of the C(2)−C(3) π-bond of **3**. Experimentally we always obtained a mixture of **8a** as the minor component and **8b** as the major product, suggesting an equilibrium between both isomers at the reflux temperature of benzene, as indicated in Scheme 3. Separation of regioisomers **8a** and **8b** was achieved by column chromatography on deactivated alumina with carbon disulfide as eluent, yielding pure cycloadduct **8b**, while **8a** was immobilized on the column and, unfortunately, no method could be developed to collect **8a** from the column. The overall yield of **8b** is 14.4% based on starting material and 68.2% based on recovered C_{60}, respectively.

Compound **8b** is an air-stable solid of green color (λ_{max} = 602 nm). The identity of **8b** is clearly established by observation of the protonated molecular ion ($m/z = 1534$, $M^+ + H$) in the FAB mass spectrum. The high stability of this protonated species is once again due to the α-carbenium stabilizing capacity of the ferrocenyl groups, analogous to what was discussed above for the cumulene **3**. Mössbauer spectroscopic data of **8b** are almost identical to those of cumulene **3**, in accord with a regular Fe(II) species, indicating no unusual charge distribution in terms of an intramolecular redox reaction resulting in a zwitterionic compound with partially oxidized ferrocenyl substituents and a fullerene radical anion

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moiety. As with other fullerene derivatives, the solubility of **8b** is quite limited, hampering its further characterization. ^{1}H NMR spectroscopy of a saturated solution in CS_2/C_6D_6 showed six multiplets for the substituted and four singlets for the unsubstituted cyclopentadienyl protons, in consonance with C_1 symmetry, but the ^{13}C NMR spectrum showed only approximately 16 broad resonances out of 60 expected fullerene signals in addition to the cyclopentadienyl signals; the resonances of the quaternary carbons of the six carbons of the former cumulene unit were not observed, even after collecting more than 200000 FIDs and with added Cr(acac)$_3$ as relaxation reagent. For a definite structure assignment, we tried for over two years to obtain suitable crystals for a single-crystal structure analysis by use of a number of solvents and a number of techniques, including cocrystallization with AgNO$_3$[41] or calix[5]arene,[42] but without success until now.

Finally we note that besides **8b** there exist only very few fullerene [2+2] cycloadducts[43,44] in comparison to the numerous [2+1], [2+3], and [2+4] cycloadducts, which form the main body of all known fullerene derivatives. Interestingly, attempting cycloaddition of C$_{60}$ with tetraphenyl[5]cumulene instead of tetraferrocenyl[5]cumulene **3** did not produce any product in reasonable yield, indicating that only very electron rich [5]cumulenes such as **3** react with fullerene. We also performed the reaction of cumulene **3** with C$_{70}$ and isolated in a similar manner as described above 20 mg of a pure product; however, its solubility was extremely low, preventing so far any spectroscopic measurements in solution.

C$_{60}$-based electroactive organofullerenes are of much current interest due to their anticipated applications in materials science, including molecular electronic devices, nonlinear optical materials, and artificial photosynthetic systems.[45–47] The presence of four redox-active ferrocenyl substituents in cycloadduct **8b** is therefore of interest in terms of the degree of electronic communication between the fullerene acceptor and the ferrocene donors mediated by the cyclobutane/olefin/butatriene subunit. In this context, Figure 5 shows the cyclic voltammetric pattern exhibited by **8b** in dichloromethane solution, at −10 °C.

From a qualitative viewpoint, it seems well conceivable that the overall picture comes from the overlapping of the response of complex **3** illustrated in Figure 2a with the well-known sequential reductions of C$_{60}$. Indeed, we must take into account that different redox-active subunits are present in **8b**, i.e., ferrocenes, cumulene, and fullerene. A preliminary examination of the comparative electrode potentials reported in Table 3 shows that (i) the first ferrocene-based oxidation is shifted toward more positive potential values by about
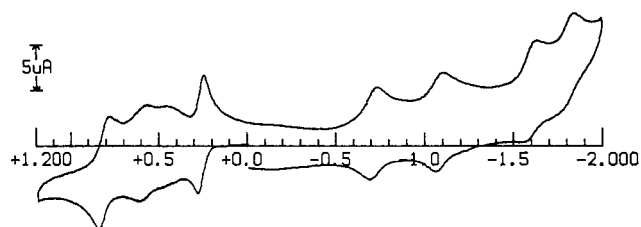

Figure 5. Cyclic voltammogram recorded at a platinum electrode on a CH$_2$Cl$_2$ solution containing [NBu$_4$][PF$_6$] (0.2 mol/L) and **8b** (7 × 10^{-4} mol/L). Scan rate 0.2 V s^{-1}. $T =$ −10 °C.

Table 3. Formal Electrode Potentials (V, vs SCE) for the Redox Changes Exhibited by 8b and Related Species, in Dichloromethane Solution, at −10 °C

compd	cumulene oxidation $E^{\circ\prime}$	ferrocene oxidation $E^{\circ\prime}$	fullerene reductions $E^{\circ\prime}_1$	$E^{\circ\prime}_2$	$E^{\circ\prime}_3$	$E^{\circ\prime}_4$	cumulene reduction $E^{\circ\prime}$
C$_{60}$			−0.63	−1.00	−1.45	−1.90	
8b	+0.82	+0.26	−0.72	−1.08	−1.83		−1.56
3	+0.83	+0.23					−1.39

30 mV with respect to that of **3**, indicating that the fullerene ligand acts, as expected, as the electron-acceptor unit; (ii) the cumulene-based oxidation is basically unaltered with respect to that of **3**; and (iii) the two first fullerene-centered reductions are shifted toward more negative potential values by about 80 mV with respect to those of free C$_{60}$. This latter shift may arise from the interruption of the extended C=C double bond conjugation of fullerene as a consequence of the coordination to the cumulene moiety and additionally from the electron donation by the ferrocenyl units. Less straightforward is the assignment of the nature of the third cathodic reduction as either a fullerene-centered or a cumulene-centered step. Based on the relative peak height, we tend to assign this third step as centered on the cumulene fragment, thus resulting in a cathodic shift of about 170 mV with respect to that of **3**. On this basis, the fourth reduction, which would correspond to the third reduction of the fullerene ligand, should be shifted toward more negative potential values by about 380 mV with respect to free C$_{60}$. Both these significant shifts could be due to the electrostatic repulsion arising from the addition of the two electrons to the cumulene−fulleride dianion or the addition of the third electron to the fulleride−cumulene tetraanion.

Summary

Tetraferrocenyl[5]cumulene is synthesized from diferrocenylmethoxypropyne by formal dimerization of the intermediate diferrocenylethenylidenecarbene. The cumulene is an electron-rich compound, as indicated by its physical and spectroscopic properties in comparison to analogous shorter cumulenes. Electrochemically, the four ferrocenyl groups concomitantly oxidize in dichloromethane solution at a single potential value, which is less positive by about 120 mV with respect to unsubstituted ferrocene, indicating substantial electron donotion from the cumulene-bridging ligand toward the peripheral electrochemically noninteracting ferrocenyl groups. Whereas shorter ferrocenyl cumulenes have been shown to be unreactive due to steric shielding by

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the four metallocenyl termini, tetraferrocenyl[5]cumulene has a rich chemistry, including transition metal complex formation and [2+2] cycloaddition with olefins, with alkynes, and, most notably, with fullerenes C_{60} and C_{70}. In addition, attempted [4]radialene synthesis by Ni(0)-promoted cyclodimerization yielded an unusual [3]-ferrocenophane by an intramolecular aromatic electrophilic substitution. The degree of electronic interaction between the ferrocenyl donors and the fullerene acceptor moiety of the [2+2] cycloadduct of tetraferrocenylcumulene with C_{60} has been investigated by cyclic voltammetry, showing that complex interactions among the three redox-active components (ferrocenyls, cumulene, and fullerene) take place, but overall the ferrocenyl groups act as electron donors and the fullerene ligand acts as an electron acceptor, as anticipated.

Experimental Section

General Comments. Standard techniques and instrumentation for spectroscopic and physical measurements have been published previously.[12,48]

1,1-Diferrocenylprop-2-yn-1-ylium Tetrafluoroborate (2a). A 50 mL round-bottom flask was charged with 50 mg (0.11 mmol) of 1,1-diferrocenyl-1-methoxypropyne[11] and 40 mL of dry ether. To the stirred solution was added 16 μL of 54% HBF$_4$ in Et$_2$O, precipitating the dark green product. After stirring for 10 min, the precipitate was filtered off on a sintered glass frit, the green solid was washed three times with small portions of Et$_2$O, and the product was dried in vacuo, yielding 40 mg (0.081 mmol, 73.6%) of **2a**.

Data for 2a: Green powder, slightly air sensitive in solution, mp 220 °C, dec. Anal. Calcd for $C_{23}H_{19}BFe_2F_4$: C, 55.93; H, 3.88. Found: C, 55.74; H, 3.86. MS (FAB): *m/z* 407.2 (M$^+$ of cation, 31%). IR (KBr): 3256w, 3108w, 2093m ($\nu_{C\equiv C}$), 1638w, 1481s, 1414s, 1386s, 1353m, 1330m, 1286s, 1036s, 951m, 832m, 793w, 706s, 594w, 559w, 521s, 497s, 476s, 452s cm^{-1}. UV−vis (CH$_2$Cl$_2$; λ_{max}/ϵ): 387/15850; 738/9330 nm. ^{1}H NMR (CD$_2$Cl$_2$, δ): 4.63 (10H, s, unsubst Cp); 5.00 (1H, s, C≡C−H); 5.39 (m, 4H, subst Cp); 5.95 (m, 4H, subst Cp). ^{13}C NMR (CD$_2$Cl$_2$, δ): 75.0 (broad, subst Cp); 78.7 (unsubst Cp); 85.4 (C(1) of subst Cp); 86.0 (subst Cp); 93.1, 93.6 (C≡C−H); 144.5 ((Fc)$_2$C$^+$).

Tetraferrocenyl[5]cumulene (3). A Schlenk vessel was charged with 125 mL of dry, deoxygenated Et$_2$O and 504 mg (1.15 mmol) of 1,1-diferrocenyl-1-methoxypropyne.[11] The orange solution was cooled to −55 °C, and 1.11 mL (1.78 mmol) of a 1.6 M methyllithium solution in Et$_2$O was added. The cooling bath was removed, and the stirred mixture was allowed to warm to room temperature. The color of the solution changed during this period from orange to dark blue. After 3 h stirring in total, TLC analysis (stationary phase, alumina; mobile phase, *n*-hexane/ether 2:1; detection of *blue* cumulene **3** by formation of *green* protonated **3**H$^+$Cl$^-$ by exposure of developed TLC plates to HCl vapor) indicated no further progress in reaction or the beginning of the formation of byproducts, respectively (Note: the reaction period was different for different preparations under otherwise identical conditions; therefore regular TLC analysis is mandatory in each case to decide on the end point of the reaction). Workup: The dark blue solution was filtered without protection from air through a short column of basic alumina, and the filtrate was reduced in volume on a rotary evaporator to 30 mL. After addition of 30 mL of *n*-hexane, the solution was concentrated on a rotary evaporator to approximately half its volume and the product precipitated. The blue solid material was filtered off immediately and washed with small portions of *n*-hexane

until no starting material and byproducts could be detected by TLC analysis in the hexane fractions. Drying in vacuo afforded 340 mg (0.42 mmol, 73%) of **3**.

Data for 3: Blue powder, air stable, mp 112 °C, dec. Anal. Calcd for $C_{46}H_{36}Fe_4$: C, 68.03; H, 4.47. Found: C, 68.12; H, 4.46. MS (FAB): *m/z* 814 (M$^+$ + 2H, 32); 813 (M$^+$ + H, 57). IR (KBr): 3091w, 2962w, 2923w, 2853w, 2005w, 1627w, 1451m, 1410w, 1401w, 1379w, 1261s, 1106s, 1053s, 1024s, 1001s, 895s, 818s, 789s, 513m, 479s, 455s cm^{-1}. FT-Raman (633 nm, 0.2 mW): 1973s (C=C=C=C=C=C), 1540s, 1436m, 1201s, 922m, 675m, 632m, 502m, 309m cm^{-1}. UV−vis (CH$_2$Cl$_2$; λ_{max}/ϵ): 234/41400; 308/14800; 380/10300; 471/14600; 478/14700; 522/15700; 624/22500 nm. ^{1}H NMR (CD$_2$Cl$_2$, δ): 4.26 (20H, s, unsubst Cp); 4.48 (m, 8H, subst Cp); 4.81 (m, 8H, subst Cp). ^{13}C NMR (CD$_2$Cl$_2$, δ): 69.3 (subst Cp); 70.2 (subst Cp); 70.4 (unsubst Cp); 85.0 (C(1) of subst Cp); 119.8 (C(1) of C=C=C=C=C=C); 119.9 (C(2) of C=C=C=C=C=C); 140.8 (C(3) of C=C=C=C=C=C). ^{57}Fe Mössbauer data (90 K): IS = 0.531 ± 0.001 mm s^{-1}; QS = 2.315 ± 0.003 mm s^{-1}. CV (CH$_2$Cl$_2$, −10 °C, V vs SCE): −1.39, +0.23, +0.83 (Table 1, Figure 2).

Tetraferrocenyl[5]cumulene−Bis(triphenylphosphine)rhodium(I) Chloride (4). A Schlenk tube was charged with 30 mL of dry, deoxygenated benzene, 40 mg (0.049 mmol) of **3**, and 56 mg (0.061 mmol) of tris(triphenylphosphine)-rhodium(I) chloride. The blue solution was refluxed under an atmosphere of Ar for 1.5 h, and a color change from blue to purple was observed. Workup: Volatile materials were removed in vacuo, the residue was dissolved in *n*-hexane, and the solution was filtered through a short column of silica to remove triphenylphosphine by repeated washings with *n*-hexane until no more triphenylphosphine could be detected by TLC analysis in the washing fractions. The product was eluted with Et$_2$O, the solvent was removed on a rotary evaporator, and the residue was dried in vacuo, yielding 35 mg (0.0237 mmol, 48.4%) of **4**.

Data for 4: Black-purple powder, air stable, mp 174 °C, dec. Anal. Calcd for $C_{82}H_{66}ClFe_4P_2Rh$: C, 66.77; H, 4.51. Found: C, 66.57; H, 4.49. MS (FAB): *m/z* 1477.6 (M$^+$ + 2H, 50); 1476.5 (M$^+$ + H, 53); 1474.5 (M$^+$, 58); 1212.4 (M$^+$ − P(C$_6$H$_5$)$_3$, 86); 1057 (M$^+$ − P(C$_6$H$_5$)$_3$ − Cl − FeCp, 69); 627.5 ([P(C$_6$H$_5$)$_3$]$_2$RhCl, 100). IR (KBr): 3056w, 2961m, 2925s, 2856m, 1732m, 1636m, 1481w, 1465w, 1436m, 1412w, 1385w, 1262s, 1106s, 1096s, 1027s, 899w, 807s, 745w, 695m, 517m, 492m cm^{-1}. UV−vis (CH$_2$Cl$_2$; λ_{max}/ϵ): 264/41100; 348/13000; 446/16300; 592/21000 nm. ^{1}H NMR (CD$_2$Cl$_2$, δ): 3.75 (5H, s, unsubst Cp); 3.79 (5H, s, unsubst Cp); 4.03 (5H, s, unsubst Cp); 4.17 (5H, s, unsubst Cp); 4.25 (m, 2H, subst Cp); 4.38 (m, 2H, subst Cp); 4.50 (m, 2H, subst Cp); 4.55 (m, 2H, subst Cp); 4.56 (m, 2H, subst Cp); 4.65 (m, 2H, subst Cp); 4.69 (m, 2H, subst Cp); 5.98 (br s, 2H, subst Cp); 7.21−7.65 (m, 30H, P(C$_6$H$_5$)$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 67.9, 68.2, 68.4, 68.5, 68.8 (subst Cp); 69.4, 69.6, 70.0, 70.1 (unsubst Cp); 70.4, 70.9 (subst Cp); 84.7, 85.5, 87.7, 89.3 (C(1) of subst Cp); 107.9 (d, *J*(^{13}C−^{103}Rh) = 14.5 Hz, cumulene); 114.0 (d, *J*(^{13}C−^{103}Rh) = 4.4 Hz, cumulene); 122.6 (d × t, *J*(^{13}C−^{103}Rh = 19.1 Hz, *J*(^{13}C−^{31}P) = 4.2 Hz, cumulene); 123.9 (d × unresolved t, *J*(^{13}C−^{103}Rh) = 2.9 Hz, *J*(^{13}C−^{31}P) = not resolved, cumulene); 128.2 (pseudo-t, *J*(^{13}C−^{31}P) = *J*(^{13}C−^{103}Rh) = 5.1 Hz, phenyl); 130.2 (s, phenyl); 132.0 (pseudo-t, *J*(^{13}C−^{31}P) = *J*(^{13}C−^{103}Rh) = 21.8 Hz, phenyl); 132.3 (d × t, *J*(^{13}C−^{103}Rh) = 6.5 Hz, *J*(^{13}C−^{31}P) = 3.6 Hz, cumulene); 135.3 (pseudo-t, *J*(^{13}C−^{31}P) = *J*(^{13}C−^{103}Rh) = 5.8 Hz, phenyl); 153.5 (broad s = unresolved d × t, cumulene). ^{31}P NMR (CD$_2$Cl$_2$, δ): 27.3 (d, ^{1}*J*(^{31}P−^{103}Rh) = 125.1 Hz). X-ray structure analysis: single crystals were obtained from Et$_2$O/*n*-hexane (Table 2, Figure 3, Supporting Information).

1,1,2,2-Tetracyano-3-(3,3′-diferrocenylallenyliden)-4-(1,1′-diferrocenylmethylidene)cyclobutane (5). A Schlenk tube was charged with 20 mL of dry, deoxygenated benzene, 42 mg (0.052 mmol) of **3**, and 7 mg (0.055 mmol) of tetracyanoethylene. The mixture was stirred for 1 h, yielding a brown solution. Workup: benzene was removed in vacuo, and the

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residue was dissolved in dichloromethane and chromatographed on basic alumina (eluent: CH_2Cl_2/n-hexane = 2:1; 0.75 mL of triethylamine was added to the eluent to ensure basic conditions), yielding 20 mg (0.021 mmol, 40.9%) of **5**.

Data for 5: Brown-green powder, air stable, mp 150 °C, dec. Anal. Calcd for $C_{52}H_{36}Fe_4N_4$: C, 66.42; H, 3.86. Found: C, 66.56; H, 3.85. MS (FAB): m/z 940.1 (M^+, 22); 663.5 ($M^+ -$ Fc $-$ Cp $-$ CN, 47); 647.5 ($M^+ -$ 2 FeCp $-$ 2 CN + H, 65); 530.6 ($M^+ -$ Fc $-$ FeCp $-$ 4 CN, 75); 441 ($M^+ -$ 2 Fc $-$ TCNE $-$ H, 100). IR (KBr): 3096w, 2957w, 2923w, 2854w, 2211w ($C\equiv N$), 1636w, 1549m, 1477s, 1452s, 1401m, 1383m, 1353w, 1317w, 1261w, 1106m, 1053m, 1004w, 823m, 732w, 717w, 481s cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 4.29 (12H, s, unsubst Cp + subst Cp); 4.34 (5H, s, unsubst Cp); 4.36 (5H, s, unsubst Cp); 4.48 (6H, br s, subst Cp); 4.71 (6H, br s, subst Cp); 5.11 (2H, m, subst Cp). ^{13}C NMR (CD_2Cl_2, δ): 32.0, 32.3 (saturated carbons of cyclobutane); 70.2, 70.3, 70.4, 70.7, 72.6, 73.5, 71.4, 72.7, 82.1, 83.3 (subst and unsubst Cp); 103.2, 114.6, 114.7, 117.4, 125.1, 125.5, 163.7, 165.8, 199.2 ($C\equiv N$, $C=C=C$, and $C=C$).

1,2-Dicarboxylic Acid Dimethyl Ester−3,4-Bis(2,2′-diferrocenylvinylidene)cyclobut-1-ene (6). A solution of 250 mg (0.31 mmol) of **3** and 0.80 mL (6.0 mmol) of dimethyl acetylenedicarboxylate in 50 mL of dry, deoxygenated benzene was refluxed under an atmosphere of Ar for 3 days. Workup: Volatile materials were removed in vacuo, and the residue was dissolved in dichloromethane and chromatographed on alumina (eluent: CH_2Cl_2/n-hexane = 1:1, 0.5 mL of triethylamine was added to the eluent to ensure basic conditions), yielding 85.8 mg (0.0899 mmol, 29%) of **6**.

Data for 6: Blue microcrystalline solid, air stable, mp 150 °C, dec. Anal. Calcd for $C_{52}H_{42}Fe_4O_4$: C, 65.45; H, 4.44. Found: C, 65.39; H, 4.45. MS (FAB): m/z 956 ($M^+ +$ 2H, 26); 955 ($M^+ +$ H, 74); 954 (M^+, 100); 833 ($M^+ -$ FeCp, 20). IR (KBr): 3091w, 2986w, 2944w, 2064s ($C=C=C$), 1701s ($C=O$), 1458m, 1432s, 1269m, 1240m, 1214s, 1106m, 1058s, 1035s, 1002m, 891m, 820s, 791m, 705m, 693m, 491s, 472s cm^{-1}. UV−vis (CH_2Cl_2; λ_{max}/ϵ): 323/21300; 379/16500; 554/19400; 669/30500; 692/27500; 750/30500 nm. ^1H NMR (CD_2Cl_2, δ): 3.91 (6H, s, CH_3); 4.22 (10H, s, unsubst Cp); 4.26 (10H, s, unsubst Cp); 4.52 (m, 4H, subst Cp); 4.60 (4H, m, subst Cp); 4.98 (8H, m, subst Cp). ^{13}C NMR (CD_2Cl_2, δ): 52.4 (CH_3); 70.7 (unsubst Cp); 70.8, 70.9, 71.4, 71.5 (subst Cp); 83.5, 83.9 (C(1) of subst Cp); 102.0, 136.6, 140.1, 154.3 ($C=C=C$ and $C=C$); 166.5 ($C=O$).

1-(1,1′-Diferrocenylallenylidene)-3-ferrocenyl-2-ene−[3]ferrocenophane (7). A solution of 42 mg (0.052 mmol) of **3** and 200 mg (0.31 mmol) of bis(triphenylphosphine)dicarbonylnickel(0) in 30 mL of dry, deoxygenated benzene was refluxed overnight under an atmosphere of Ar, and the original blue color of the reaction mixture changed to red. Chromatographic workup (basic alumina, n-hexane/Et_2O = 20:1) yielded 15 mg (0.0185 mmol, 35.5%) of **7**.

Data for 7: Red crystals, air stable, mp 140 °C, dec. Anal. Calcd for $C_{46}H_{36}Fe_4$: C, 68.03; H, 4.47. Found: C, 67.95; H, 4.46. MS (FAB): m/z 814 ($M^+ +$ 2H, 57); 813 ($M^+ +$ H, 100); 691.5 ($M^+ -$ FeCp, 8). IR (KBr): 3087m, 2964w, 2923w, 2854w, 2038w, 1713m, 1654m, 1638m, 1590m, 1412m, 1378m, 1262s, 1104s, 1057s, 1026s, 1001s, 820s, 807s, 490s, 482s, 473s cm^{-1}. UV−vis (CH_2Cl_2; λ_{max}/ϵ): 286/11100; 426/22600; 550/14500 nm. ^1H NMR (CD_2Cl_2, δ): 4.13 (5H, s unsubst Cp); 4.17 (5H, s, unsubst Cp); 4.37 (9H, m, subst and unsubst Cp); 4.32 (4H, m, subst Cp); 4.35 (2H, m, subst Cp); 4.39 (4H, m, subst Cp); 4.45 (2H, m, subst Cp); 4.62 (2H, m, subst Cp); 4.78 (2H, m, subst Cp); 6.94 (1H, s, $CH=C$). ^{13}C NMR (CD_2Cl_2, δ): 66.9, 69.2, 69.5, 69.6, 69.8, 69.9, 70.0, 70.1, 70.2, 72.1, 84.8, 86.9, 87.0 (subst and unsubst Cp); 88.1, 108.8, 120.8, 133.6, 134.2, 139.9 ($C=C=C=C$ and $CH=C$). X-ray structure analysis:

single crystals were obtained from Et_2O/CH_2Cl_2 (Table 2, Figure 4, Supporting Information).

Cyclobuta[1,9][5,6]fullerene−C_{60}−I_h−2′-(3,3′-Diferrocenylallenylidene)-3′-(1,1′-diferrocenylmethylidene) (8b). A 250 mL Schlenk flask was charged with 150 mg (0.208 mmol) of C_{60}, 169 mg (0.208 mmol) of **3**, and 100 mL of dry deoxygenated benzene. The mixture was refluxed under an atmosphere of Ar for 15 h. After no more cumulene **3** could be detected by TLC analysis, the reaction was terminated and worked up: Solvents were removed in vacuo, the residue was dissolved in carbon disulfide, the solution was filtered through a very short column of basic alumina to remove CS_2-soluble unreacted fullerene (118 mg, 0.164 mmol) while the products remained immobilized on the alumina, the products were eluted with dichloromethane from the alumina column, the dichloromethane solution was evaporated, and the residue was dissolved in carbon disulfide and chromatographed on a long column of deactivated neutral alumina (Brockmann activity III) with CS_2 as the mobile phase. The product **8b** displays a *blue* color while on the column, whereas in solution a *green* color is observed. During the chromatography the column becomes slightly yellow-brown, indicating permanent immobilization of the product **8a** on the alumina; unfortunately no solvent could be found that is capable of recovering product **8a** from the column. In this manner, 46 mg (0.03 mmol, 14.4% based on 0.208 mmol starting materials, 68.2% based on recovered C_{60}) of pure **8b** was obtained.

Data for 8b: Green powder, air stable, mp >200 °C, dec. Anal. Calcd for $C_{106}H_{36}Fe_4$: C, 83.06; H, 2.37. Found: C, 83.31; H, 2.34. MS (FAB): m/z 1534.1 ($M^+ +$ H, 5); 1292.1 ($M^+ -$ 2Cp + H, 6); 811.9 ($M^+ -$ C_{60}, 91); 720 (C_{60}, 100). IR (KBr): 3097w, 2954m, 2923m, 2854m, 1719w, 1686w, 1630m, 1561w, 1461w, 1412w, 1262m, 1183w, 1108m, 1059m, 1001m, 818m, 592w, 577w, 563w, 527m, 484m cm^{-1}. UV−vis (CH_2Cl_2; λ_{max}/ϵ): 254/112200; 316/49000; 602/10200 nm. ^1H NMR (CS_2/C_6D_6 = 4;1, δ): 4.00 (5H, s unsubst Cp); 4.02 (5H, s, unsubst Cp); 4.20 (5H, s, unsubst Cp); 4.22 (3H, m, subst Cp); 4.31 (5H, s, unsubst Cp); 4.47 (2H, m, subst Cp); 4.49 (3H, m, subst Cp); 4.70 (3H, m, subst Cp); 4.78 (2H, m, subst Cp); 5.03 (3H, m, subst Cp). ^{13}C NMR (o-CCl_2D_4, Cr(acac)$_3$, δ): 69.9, 70.1, 70.16, 70.19, 70.4, 70.5, 70.7, 70.9, 71.5 (Cp); 134.3, 134.8, 134.9, 135.2, 135.5, 137.1, 137.5, 137.8, 140.6, 142.1, 142.6, 142.7, 142.8, 144.3, 145.0, 145.8 (fullerene). ^{57}Fe Mössbauer data (90 K): IS = 0.532 ± 0.001 mm s^{-1}; QS = 2.347 ± 0.001 mm s^{-1}. CV (CH_2Cl_2, −10 °C, V vs SCE): −1.83, −1.56, −1.08, −0.72, +0.26, +0.82 (Table 3, Figure 5).

Supporting Information Available: Tables of crystal data and structure refinement details, anisotropic thermal parameters, fractional atomic parameters, isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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